Standard Operating Procedure for Sampling of Particulate Phase Mercury

Gerald J. Keeler and Matthew S. Landis
University of Michigan
Air Quality Laboratory
109 South Observatory Street
Ann Arbor, MI 48109-2029

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1.0 Introduction/Overview

The objective of the Lake Michigan Loading Study is to assess the contribution of atmospheric deposition to the concentration of mercury and other toxic trace species found in Lake Michigan. The atmosphere has been implicated as one of the dominant sources of mercury and trace elements to bodies of water and it is clear from investigations in remote regions of the globe that long range transport of mercury and other toxics from source regions is occurring. By quantifying the wet deposition and ambient concentrations of mercury it will be possible to determine the relative importance of precipitation and dry deposition in accounting for the atmospheric loading of mercury to Lake Michigan. In addition, investigating other ambient trace species will aid in the identification of significant mercury sources.

Particle-phase mercury, Hg(p), generally represents a small but significant fraction of total atmospheric mercury. Recent advances in analytical chemistry have made quantification of the extremely low levels of Hg(p) possible, however, tremendous care must be exercised in all phases of sample handling and analysis. This protocol describes analysis of 'acid-extractable' total mercury from atmospheric particulate samples.

2.0 Preparation for Particulate Mercury Sampling

2.1 Acid Cleaning Procedure

All field sampling and analytical supplies which will come into contact with the samples are cleaned according to the following procedure.

Supplies to be acid cleaned are first rinsed in reagent grade acetone under a fume hood, then washed in hot tap water and diluted Alconox. Supplies are rinsed five times in cold tap water then rinsed three times in DI water. The supplies are then heated in 3M hydrochloric acid (EM Science Tracepur HCl in Milli-Q water (18.2 MÙ/cm)) for six hours at 80°C. One liter of 3M HCl is prepared by adding 750 mL of Milli-Q water to 250 mL of concentrated EM Science Tracepur HCl. The 3M HCl can be used several times and is stored for reuse in a polyethylene carboy dedicated for this purpose. The supplies are placed into clean polyethylene tubs which are then filled with the 3M HCl, making sure that all of the surfaces are submersed in the HCl. The tubs are covered and placed in a water bath which is heated to 80°C in a fume hood. The water in the bath is maintained at the level of the acid inside the tubs. After the water in the bath reaches 80°C, the supplies in the tubs are allowed to soak for six hours.

After the six hours, 80°C soak, the tubs are removed from the water bath and allowed to cool in the fume hood. When cool, the 3M HCl is poured back into its polyethylene carboy. The supplies are rinsed in the tubs three times with Milli-Q water. The supplies are then soaked in a 0.56M nitric acid solution (Baker Instra-Analyzed HNO_3 in Milli-Q water) for 72 hours at room temperature in the same polyethylene tubs in which they were heated with HCl. The nitric acid

solution is made by adding 35 mL Baker Instra-Analyzed HNO_3 to 965 mL of Milli-Q water. Nitric acid is reused for up to 6 months and is stored in a carboy dedicated for HNO_3. At the end of the three-day soak, the supplies being cleaned are rinsed three times with Milli-Q water and transferred into a Class 100 Clean Room.

Inside the clean room, the supplies are again rinsed three times with Milli-Q water. The tubs containing the supplies are filled with 0.56M Baker Instra-Analyzed HNO_3 that is kept in the clean room and is dedicated for this final step only. The supplies are then allowed to soak in this acid for seven days. This acid is prepared by adding 35 mL of the Instra-Analyzed HNO_3 to 965 mL of Milli-Q water. At the end of the seven day acid soak inside the clean room, the supplies are rinsed five times with Milli-Q water and allowed to air dry on a clean surface. When the supplies are dry, they are triple bagged in new polyethylene bags and removed from the clean room, ready for use in sampling.

2.2 Preparation of Glass Fiber Filters

Glass fiber filters (Gelman Sciences) are pre-treated to remove all mercury prior to use in sampling. Glass fiber filters, 47 mm in diameter, are placed in a clean crucible with a lid. The crucible is placed in a muffle furnace which is heated to 500°C and the filters are allowed to bake at this temperature for one hour. While hot, filters are removed from the crucible with acid-cleaned Teflon-coated forceps and placed in an acid-cleaned Teflon jar which is closed and sealed with Teflon tape. The Teflon jar is sealed in three successive polyethylene bags and stored at 40°C until use. Filters are stored no more than three months prior to use and frequent blanks are taken to ensure the filters remain clean.

3.0 Particulate Phase Mercury Sample Collection

During sample collection the filter packs are housed in a sampling box that is mounted on a pole or tower at least 3 meters above ground level. The sampling boxes are custom-made at UMAQL from fiberglass enclosures (Stahlin Enclosures) using quick connect couplings to connect the vacuum lines from the pump to the sampling devices. Sample intakes are at least 30 cm apart and are not close to any potential contaminant sources.

Since particulate mercury occurs at ultra-trace levels in the atmosphere and since mercury has a high vapor pressure, the selection of sampling flow rate and sampling duration has been carefully considered. It is typically necessary to sample at flow rates of 10-30 lpm for a minimum of 12-24 hours to collect enough particulate mercury for analysis.

The volume of air sampled is measured using a calibrated dry test meter (DTM). In addition, the flow rate is confirmed at the sample inlet before each sample using a calibrated rotameter. The pumps used (URG-3000-02M) are specially designed for trace level mercury sampling. They feature high efficiency oil less, brush less pumps. All pumps used for sampling are turned on at least 15 minutes prior to use.

3.1 Setting Up Glass Fiber Filter Samples

All sample preparation including filter pack assembly is done outdoors. In extreme weather conditions, operators may elect to complete some tasks in a clean indoor area, making sure sampling supplies (filter packs, forceps etc.) do not contact any surfaces other than in the clean bags in which they were received. Particle free gloves are worn during all sampling activities. When outdoors, site operators position themselves downwind of the sample at all times.

Before sampling commences, it is necessary to confirm the flow rate through the sampling train using a calibrated 30 lpm rotameter. To prevent potential contamination of the sample by the rotameter a 'flow check' filter pack is utilized. The 'flow check' filter pack is equipped with quick connects on either side for attachment of the vacuum line and the rotameter. The glass fiber filter in the 'flow check' filter pack is changed on a regular basis because is will rip or tear over time. The 'flow check' filter pack is placed into the mercury sampling box (Appendix B) such that the orange clampdown nut is on the inside of the mercury sampling box. The male quick-connect on the designated black latex vacuum line for the particulate mercury sample is secured into the female quick-connect on the back of the 'flow check' filter pack. An audible click is heard when the quick-connects are properly sealed.

The calibrated 30 lpm rotameter is equipped with an air diffusion muffler at the inlet and a 22 cm length of black latex tubing with a male quick connect at the outlet. The male quick connect on the rotameter tubing is connected to the female quick connect on the inlet of the test flow filter pack. The system is allowed to stabilize before taking the reading from the rotameter. The scale on the rotameter is read from the midpoint of the silver ball. The calibration curve and 30 lpm set point are indicated on the side of the rotameter. If the flow is below 30 lpm the operators are referred to the trouble shooting section (3.4) to look for possible remedies. If all systems appear normal, the operator adjusts the pump flow as necessary to achieve 30 lpm before starting the sample. The rotameter and 'flow check' filter pack are then removed and stored it in the plastic box provided.

Note: Once set, the flow on the URG-3000-02M is relatively stable. If frequent adjustments are necessary to achieve the desired flow operators are instructed to contact Matthew Landis at UMAQL immediately.

An 'open face' Teflon filter pack is utilized by UMAQL for particulate phase mercury collection. The filter pack is an assemblage of three main components--a threaded 47 mm opaque Teflon cylinder, a circular opaque Teflon filter support base with a 0.64 cm tube ferule nut, and an orange Teflon clamp down nut. After confirming the flow rate to be 30 lpm an acid-cleaned Teflon 'open-face' filter pack is removed from the field site box and unbagged. The filter pack is disassembled by unscrewing the orange clampdown nut and removing the 47 mm Teflon cylinder. The Teflon jar holding the pre-baked glass fiber filters is carefully opened. One 47 mm baked glass fiber filter is placed on the grid of the filter holder with the 'rough' side up using acid-cleaned Teflon-coated forceps. While holding the filter support base vertically to prevent the filter from falling out, the filter pack is reassembled by attaching the 47 mm Teflon tube and threading it firmly into the orange clampdown nut. The Teflon jar holding the remaining pre-baked glass fiber filters is quickly closed. Operators attempt to have the jar open for as little time as possible.

The sample filter pack is then inserted into the mercury sampling box hole designated for the particulate mercury sample. The quick-connect from the vacuum line to the outlet of the filter pack is secured. The DTM reading is immediately recorded along with the time, sample number, date, unusual meteorological conditions and any problems encountered on the sample log and tracking form.

3.2. Taking Down Glass Fiber Filter Samples

After putting on a new pair of particle free gloves, the black latex vacuum line is disconnected from the sample filter pack by uncoupling the quick connectors. The DTM reading is immediately recorded, along with the time, date, unusual meteorological conditions and any problems encountered, on the sample log and tracking form. The sample filter pack is removed from the mercury sampling box. While holding the filter pack vertically with the open tube facing up, the Teflon inlet cylinder is unscrewed from the orange clampdown nut. The Teflon cylinder is removed and the filter support base is lightly pushed up until the glass fiber filter is just below the top of the orange clampdown nut. The filter is then removed from the filter support base with acid-cleaned Teflon-coated forceps, making sure to only touch the exterior edge of the filter. The filter is carefully inserted into the base of the petri dish. The petri dish cover is replaced and sealed with a length of 1.27 cm Teflon tape around the joint between the lid and the base of the petri dish. The sample identification label is then attached to the cover of the petri dish. The sample filter pack is reassembled and sealed in a clean polyethylene bag and stored in the plastic container provided. The petri dish is triple bagged and shipped to UMAQL the day they it is collected. If the operator is unable to ship the sample, the sample is placed in a freezer until it can be shipped the next day.

3.3. Taking Blanks

A minimum of 25% field blanks and 10% storage blanks are taken to ensure samples are being collected in a contaminant-free manner. Field blanks involve loading a glass fiber filter into the open-face filter pack as described in Section 3.1 for a sample. The filter pack is placed in the mercury sampling box for two minutes *without the vacuum line attached*. After two minutes, the sample is taken down and labeled in the same manner as described in Section 3.2 for samples. Storage blanks are collected by transferring a new, unexposed filter from the Teflon jar into an acid-clean petri dish. The petri dish is sealed with Teflon tape and labeled appropriately. Blanks are shipped to UMAQL along with the samples taken on the same date.

3.4 Trouble Shooting

If flow through the 'flow check' filter pack is low:

- Check to make sure that all the connections are sealed (make sure the 'flow check' filter pack ferule nut fitting is tight, tubing quick connectors are all properly fastened, filter pack is screwed together tightly, tubing from the pump to the sampler is intact and connected securely).

- Make sure that the exhaust of the rotameter is not impeded in any way when using the rotameter to check flow.

- Check the vacuum gauge on the URG-3000-02M. If a high vacuum is indicated, quickly turn off the pump and look for a kink in the tubing or an obstruction in the exhaust tubes.

- Check the black latex tubing in the sampling box for cracks or tears due to weathering.

If all systems seem to be working properly and the flow remains low or erratic the operators are instructed to notify Matthew Landis at UMAQL (313) 763-7714 or at home (313) 663-9615 immediately.

4.0 Clean Room Procedures

4.1 Entering the Clean Room

Shoes are taken off outside the clean room by all UMAQL personnel. Personnel then enter the outer vestibule (changing room). Once inside, the hood is put on followed by the clean room suit and clean room boots. The boots are snapped to the suit at the back of the leg (to hold up the boots) and are buckled in the front. Personnel then step over a dividing bench where they put on clean room gloves and snap the clean room suit at the wrist. Now fully clothed they enter the clean room making sure to securely close the door behind.

4.2 Taking Supplies into the Clean Room

All supplies to be taken into the clean room are double bagged in polyethylene. The supplies to be taken into the clean room are placed in the outer dressing room. Upon entering the clean room, the outer bag is removed and left in the entry room. All supplies that enter the clean room that have not been bagged are rinsed with MQ-water and wiped off with particle-fee wipes.

5.0 Performance Criteria, Quality Assurance and Quality Control

5.1 Field operators are carefully instructed in the techniques of contaminant-free particulate phase mercury sample collection. All of the operators are currently operating sampling equipment for either the National Dry Deposition Network, the National Atmospheric Deposition Program, the Integrated Atmospheric Deposition Network or the Great Lakes Acid Deposition Network.

5.2 Every six months UMAQL personnel inspect each of the sampling sites to audit the performance of the equipment and to make all necessary repairs or adjustments.

5.3 Co-located samples are collected from one sampling site during the study to quantify method precision. Reported concentrations for co-located samples are based on the mean of the two samples.

5.4 Precision and accuracy levels will be set and maintained for each type of analysis. A relative precision for total mercury of less than 15% is maintained for samples with values at least three standard deviations greater than the detection limit. Analysis of standards and controls is within 10% of the stated value.

A minimum of 25% of all samples are analyzed in duplicate. Reported concentrations are based on the mean of the replicates. Analytical precision averages better than 6%.

5.5 Every three months maintenance on the CVAFS analyzer is conducted, including replacement of the UV lamp, the Teflon tubing, and the detection cell.

Appendix A. Facilities, Equipment and Reagents

Following is a list of the required facilities, equipment, supplies and reagents for sample preparation and sample collection that are outlined in this document. The make and model of the following items are those used at The University of Michigan Air Quality Laboratory. Many of these items are available from a variety of sources.

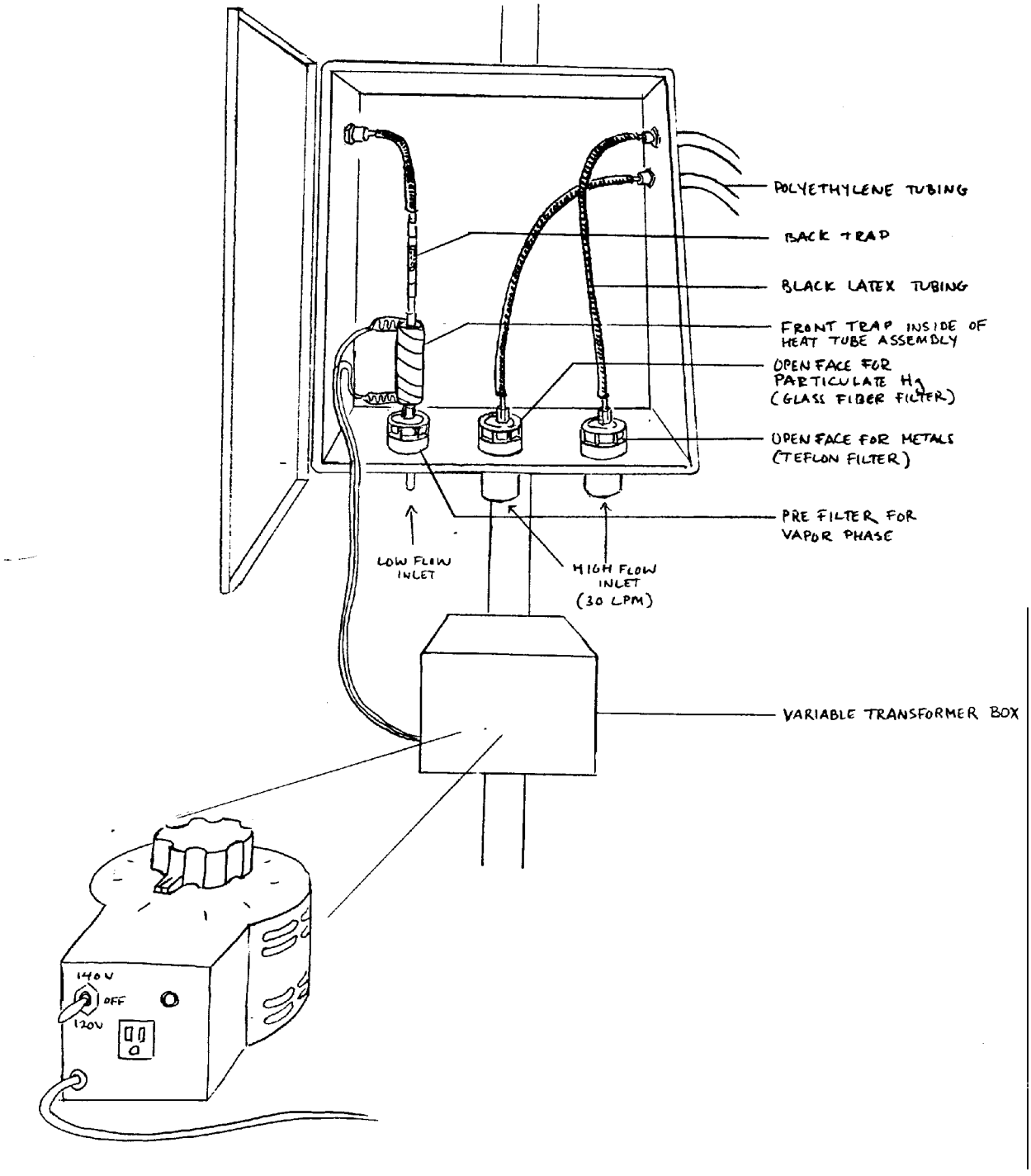
1. Preparation of Field Supplies

- Class 100 Clean Room, Work Stations
- Clean Room Gloves
- Particle-free Wipes
- Clean Room Cap, Gown and Boots
- Milli-Q Water (18.2MÙ/cm)
- Exhaust Hood
- Acetone
- Alconox
- Polyethylene Tubs
- EM Science Tracepur and Suprapur Hydrochloric Acid
- Polytherm Water Bath (Science/Electronics)
- Baker Instra-Analyzed or EM Science Suprapur Nitric Acid
- New Polyethylene Bags
- 20 L Polyethylene Carboys

2. Sample Collection

- Vacuum Pump (URG, Model 3000-02M)
- Calibrated Dry Test Meter (DTM)
- Calibrated 30 lpm Rotameter (Matheson)
- HDPE Tubing with quick connects
- Black Latex Tubing
- Mercury Sampling Box (UMAQL, See Appendix B)
- Acid-Cleaned 47mm Teflon Filter Holders (Savillex, PFA Labware)
- 47mm Preheated Glass Fiber Filters (Gelman Sciences A/E)
- Acid-Cleaned Teflon Jars (Savillex, PFA Labware)
- Teflon-Coated Forceps
- Particle-Free Gloves
- Teflon Tape
- Sample Labels
- Field Operator Log Book
- Sample Tracking Forms
- Shipping Boxes

Appendix B.


POLYETHYLENE TUBING
BACK TRAP
BLACK LATEX TUBING
FRONT TRAP INSIDE OF HEAT TUBE ASSEMBLY
OPEN FACE FOR PARTICULATE Hg (GLASS FIBER FILTER)
OPEN FACE FOR METALS (TEFLON FILTER)
PRE FILTER FOR VAPOR PHASE
LOW FLOW INLET
HIGH FLOW INLET (30 LPM)
VARIABLE TRANSFORMER BOX
140V
OFF
120V

Appendix C.

LAKE MICHIGAN LOADING STUDY

IIT-CHICAGO

Open-Face Filter Pack: Particulate Mercury Filter (Glass Fiber)

Sample No.	Date On	Time On	Flow On (LPM)	DTM On	Date Off	Time Off	DTM Off	Notes	Init.

PUMP SYSTEM USED:__________

DTM #:__________

ROTAMETER #:__________ CALIBRATION CURVE=__________

Appendix C. (Cont'd)

LAKE MICHIGAN LOADING STUDY *SAMPLE TRACKING FORM*

ITT--CHICAGO

Particulate Mercury Samples: Glass Fiber Filter

Sample Number*:_____
Gold Trap Number:_____
Operator:_____

Date On:_____ Date Off:_____
Time On:_____ Time Off:_____
Rotameter Reading On:_____ Rotameter Reading Off:_____

*If Blank Sample Note Type and How It Was Handled (Shipping Blank, Field Blank, etc.)

_____

Notes: (ambient conditions, anything out of the ordinary, using freshly cleaned filter packs, etc.)

_____

For Use at Univ. Of Michigan Air Quality Lab

Date Sample Received:_____ Rec'd By:_____

Date Sample Analyzed:_____ Rec'd By:_____

Analyzer #:_____

Notes: (Appearance of Sample, Are Endplugs Teflon-taped, etc.)